Applied Catalysis A, General 620 (2021) 118173

Contents lists available at ScienceDirect

Applied Catalysis A, General

journal homepage: www.elsevier.com/locate/apcata

Spicing up olefin cross metathesis with the renewables estragole and methyl sorbate

Leonildo A. Ferreira *, Josiane T. Silva, Raissa G. Alves, Kelley C.B. Oliveira, Eduardo N. dos Santos *

Department of Chemistry, Federal University of Minas Gerais, Av. Antônio Carlos, 6627, Belo Horizonte, 31270-901, Brazil

ARTICLE INFO

Keywords:
Ruthenium catalyst
Olefin metathesis
Sustainable chemistry

ABSTRACT

Diene moieties conjugated to a carbonyl group are ubiquitous in nature and are present in compounds with relevant biological properties. Herein we investigate the cross metathesis (CM) of the renewable cross partners estragole and methyl sorbate (MeSo) to produce methyl 6-(4-methoxyphenyl)hexa-2,4-dienoate. By the judicious choice of the ruthenium-based metathesis catalysts, as well as the reaction conditions, it was possible to obtain good conversion and selectivity for the desired product in catalyst loadings as low as 50 ppm (0.005 mol%), with a minimal amount of solvent.

1. Introduction

Olefin metathesis is currently a well-developed methodology for the elaboration of a diversified number of molecules containing C—C double bonds, ranging from simple commodity structures to more complex and elaborate pharmaceutical ingredients [1,2]. In particular, olefin metathesis has been employed as a powerful strategy to access functionalized olefins with high atom-economy, mild reaction conditions, and enabling the use of substrates containing electron-rich as well as several electron-deficient C—C double bonds. Illustrative examples of the latter class of substrates include cross metathesis (CM) reactions of fatty acids compounds with acrylic acid [3,4] or maleic acid [5–8] derivatives, providing access to monomer and detergent ingredients, as well as the CM of essential oils components in the preparation of high value-added fine chemicals [9–12]. Much less effort has, however, been devoted for the preparation of conjugate dienoates (and other conjugated carbonyl dienes) using olefin cross metathesis [13–19].

Molecules containing a dienyl moiety conjugated to a carbonyl group (*e.g.*, 2,4-dienoates and 2,4-dienamides) are frequently encountered in nature (Fig. 1), many possessing interesting and diverse biological properties [20–23].Moreover, molecules containing conjugated dienes to a carbonyl group find extensive use as synthetic intermediates [24–36].

Piperovatine, piperine and piperlonguminine, active ingredients found in plants of the genus *Piper*, exhibit a wide range of biological activity, including anticancer, anti-inflammatory, anti-angiogenic, anti-atherosclerotic, antimicrobial, insecticidal, anti-depressant, neuro and cardiovascular protective properties, to cite a few [37,38]. These are examples of molecules which synthesis would benefit from a cross metathesis approach, using naturally occurring allylbenzenes (*e.g.*, estragole and isosafrole) and a conjugated carbonylated-diene molecule, such as methyl sorbate. Reported herein is, therefore, a detailed investigation on the cross metathesis of renewable estragole with methyl sorbate, catalysed by ruthenium-based, second-generation metathesis catalysts (Fig. 2), in the preparation of a dienoate ester, structurally analogous to piperovatine [39].

2. Experimental section

2.1. General procedures

All manipulations of air/moisture sensitive materials were performed in a MBraun dry box filled with purified argon. All solvents were purchased in high purity grades. Anhydrous Sure-seal toluene was purified using a MBraun solvent purification system and stored in a dry box under argon atmosphere. Catalysts were obtained from Sigma-Aldrich (G2 – CAS 246047−72-3, HG2 – CAS 301224−40-8, G2-^{i}Pr – CAS 373640−75-6, and HG2-^{i}Pr – CAS 635679−24-2), Umicore (Ind2 – CAS 536724−67-1, HG2-tolyl – CAS 927429−61-6 and HG2-Mes^{R} – CAS 1025728−57-7) or Evonik (RF-2 – CAS 1190427−49-6). Estragole (98 % purity) and undecane (99 % purity) were purchased from Sigma-Aldrich, distilled in a Kugelhohr apparatus, collected under an argon

* Corresponding authors.
E-mail addresses: leonildo.laf@gmail.com (L.A. Ferreira), nicolau@ufmg.br (E.N. dos Santos).

https://doi.org/10.1016/j.apcata.2021.118173
Received 17 February 2021; Received in revised form 5 April 2021; Accepted 21 April 2021
Available online 22 April 2021

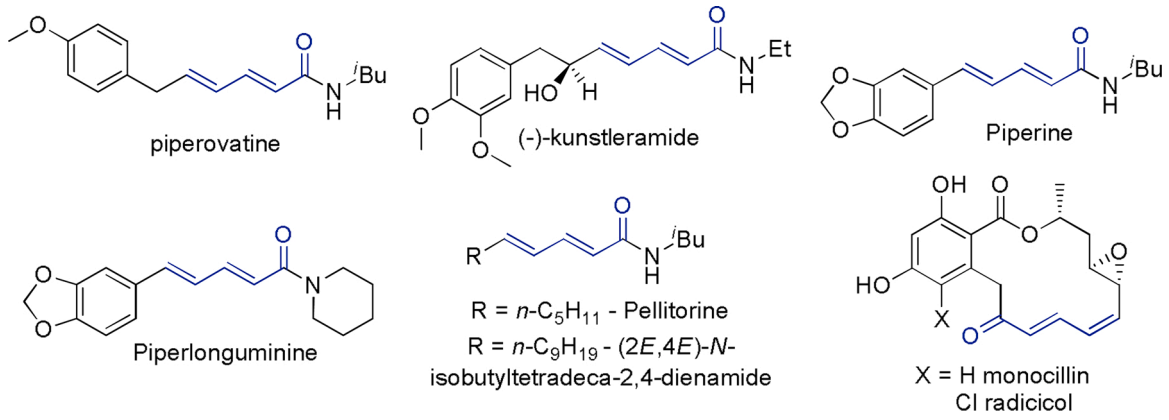


Fig. 1. Selected examples of naturally occurring molecules containing a dienic moiety conjugated to a carbonyl group.

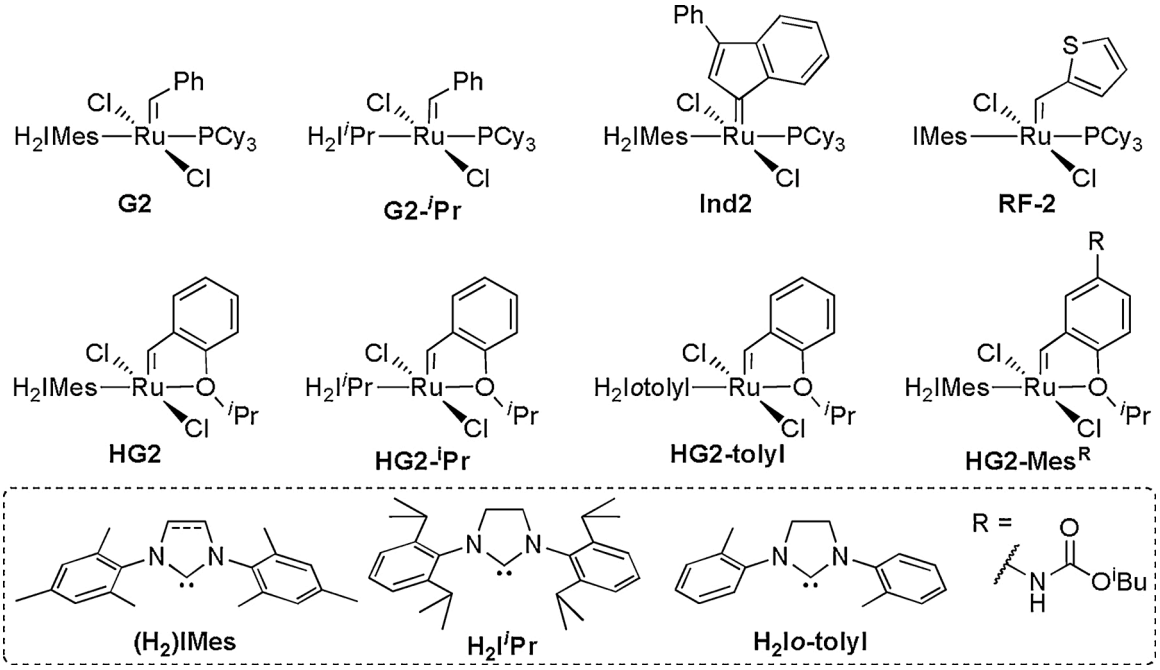


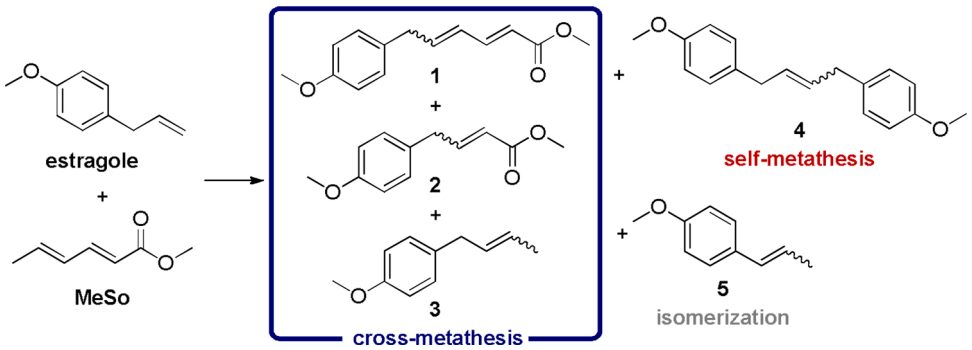
Fig. 2. Ruthenium-based olefin metathesis catalysts used for the CM of estragole with MeSo.

atmosphere, and stored in a dry box over 4 Å molecular sieves. 2,4-Hexadienoic acid was purchased from Sigma-Aldrich and used as received. The synthesis of methyl 2,4-hexadienoate (methyl sorbate) is described in the Supporting Information. NMR spectra were recorded on a Bruker Avance DRX-400 spectrometer. Chemical shifts are given in parts per million and are referenced against the solvent residual signal ($CDCl_3$ = ^{1}H NMR: 7.26 ppm; ^{13}C NMR: 77.16 ppm). GC analyses were run on a Shimadzu *2010Plus* apparatus equipped with an SH-Rtx-Wax column (30 m, 0.25 mmID, 0.25 d_f) and an FID detector. Mass spectra were recorded in a GC2010/QP2010-GC/MS apparatus with an electron impact detector at 70 eV. The temperature program for GC analysis is specified in the Supporting Information.

2.2. Protocols for the CM reactions

CM reactions were prepared inside the dry box in a reactor with seven compartmentalized wells (HEL7), each one containing 20 mL glass vials. A PTFE-coated magnetic stirring bar and a tailor-made PTFE gasket (to prevent cross-contamination) were added in each vial. The reactor lid contains seven internal condenser tips that partially enters each of the glass vials. An internal hole in the lid allows the continuous removal of volatiles by sweeping with a constant argon flow. For a picture of the reactor, refer to the SI file (Fig. S2). Each glass vial was loaded with estragole (125 μL, 0.82 mmol, 1 equiv.), MeSo (220−1100 μL, 1.68–8.4 mmol, 1–10 equiv.), undecane (internal standard for GC analysis, 200 μL, 0.95 mmol) and the reaction solvent. A 200 μL aliquot was taken (t =0 h) and then an appropriate amount of the catalyst was added as a freshly prepared stock toluene solution of precisely known concentration (typically 100−1000 μL, totalizing 5 mL of solvent in each vial). The reactor was tight-closed and taken out of the dry box and put in a pre-heated aluminium block. A mixture of water/ethylene glycol at 5 °C was circulated into the condenser tips and a steady argon flow was applied to sweep off the volatiles. Upon completion, the reaction was exposed to air to quench any remaining catalytically active specie. 200 μL of each reaction vial were diluted with 1.0 mL of untreated acetonitrile for CG analysis. Products **1** and **4** were purified by column chromatography (SiO_2, hexane/ethyl acetate 94:6). Products **2** and **3** were identified by mass spectrometry (SI), and in the case of **2**, comparison with previous reported data [9]. Product **5** (anethole), was identified by co-injection of a pure, commercial, sample.

Kinetic monitoring – In a dry box a three-neck glass round-bottom flask was loaded with estragole (250 μL, 1.64 mmol, 1 equiv.), MeSo



Scheme 1. Cross metathesis of estragole with methyl sorbate (MeSo).

Table 1
G2 loading optimization in the CM of estragole with MeSo.[a].

Entry	G2 (ppm)	Conv. (%)[b,c]	TON[d]	Selectivity (%)[c,e]			
				1 (*E,E/E,Z*)	3	4	5
1	1000	90	900	60 (23/1)	19	9	10
2[f]	1000	87	870	57 (25/1)	19	11	10
3	500	86	1720	58 (22/1)	19	12	9
4	200	79	3950	57 (18/1)	20	15	5
5	100	69	6900	55 (15/1)	19	17	6
6	70	63	9000	56 (14/1)	19	17	6
7	50	51	10,200	53 (13/1)	20	20	6

[a] Estragole (125 μL; 0.82 mmol, 1 equiv.), MeSo (440 μL; 3.28 mmol, 4 equiv.), estragole:MeSo molar ratio = 1:4, undecane (200 μL), G2 (0.82−0.041 μmol; 1000−50 ppm), toluene (5.0 mL), 60 °C, 4 h.
[b] Conversions are based on estragole.
[c] Values are within ± 2 % deviation for duplicate reactions.
[d] TON = (mol of estragole converted)/(mol of catalyst).
[e] The selectivity of **2** remained within 1–3 % for all the reactions. [f] HG2 was used instead of G2.

Table 2
Cross metathesis of estragole with different amounts of MeSo.

Entry	Equiv. of MeSo	Conv. (%)[b,c]	TON[d]	Selectivity (%)[c,e]			
				1 (*E,E/E,Z*)	3	4	5
1	2	45	9000	49 (14/1)	18	27	4
2	4	51	10,200	53 (13/1)	20	20	6
3	6	60	12,000	53 (12/1)	23	13	8
4	8	64	12,800	53 (11/1)	25	11	9
5	10	69	13,800	55 (11/1)	25	9	10

[a]Estragole (125 μL; 0.82 mmol, 1 equiv.), MeSo (220−1100 μL; 1.68–8.2 mmol, 2–10 equiv.), estragole:MeSo molar ratio = 1:2−1:10, undecane (200 μL), G2 (0.041 μmol; 50 ppm), toluene (5.0 mL), 60 °C, 4 h.
[b] Conversions are based on estragole.
[c] Values are within ± 2 % deviation for duplicate reactions.
[d] TON = (mol of estragole converted)/(mol of catalyst).
[e] The selectivity of **2** remained within 1–3 % for all the reactions.

(1320 μL; 9.84 mmol, 6 equiv.), estragole:MeSo molar ratio = 1:6, undecane (400 μL) and toluene (0.2 mL). A 10 μL aliquot was pipetted for GC analysis and the reactor was fitted to a reflux condenser under Ar. After temperature stabilization (50 °C), 800 μL of a 205 μmol L^{-1} G2 (164 μmol, 100 ppm) toluene solution was added *via* syringe to the reactor. Aliquots (10 μL) were taken after several time intervals, diluted with untreated acetonitrile, and analysed by GC-FID.

3. Results and discussion

The cross metathesis (CM) of estragole with methyl sorbate (MeSo) may result in the formation of different CM products, depending upon which MeSo C—C double bond reacts with the propagating alkylidenic specie to form a CM product. That is, either the α,β- or the γ,δ-unsaturations (Scheme 1) can coordinate to the ruthenium centre and lead to different CM products. The γ,δ-C = C is less hindered and less electron-deficient, than the α,β-C = C and is expected to react preferably with the propagating species leading the formation of **1** in detriment of **2**. The coupling of estragole in the γ,δ-position of MeSo can occur in two fashions, one with the ester moiety leading to product **1** and another with propylidene moiety leading to the CH_3-homologation of estragole (product **3** in Scheme 1). Both ways lead to two stereoisomers (*E* and *Z*). Estragole self-metathesis is also an important concurrent pathway and results in **4**. Moreover, C—C double bond isomerization of estragole can also take place, leading to **5**.

Initial experiments exploring the CM of estragole with MeSo were conducted in a 7-well compartmentalized reactor, employing the second-generation Grubbs metathesis catalyst (G2) in toluene, an estragole to MeSo molar ratio of 1:4, at 60 °C for 4 h. Volatiles formed in the reactions were swept-off with a continuous flow of argon. The variation in the catalyst loadings from 1000 to 50 ppm (1.0 to 0.005 mol % *versus* estragole) afforded an augmented turnover number from 900 to 10,200, respectively, although resulting in a gradual decrease in the conversion and affecting the selectivity for all the products. Enoate CM product **2** was formed only in minor amounts (less than 3 % selectivity) in the range of reaction conditions employed, diverging from reported data for the CM of MeSo or Weinreb dienamides with a variety of CM-partners [14]. Such a difference is likely due to the much lower catalyst loadings used in the current study (1.0−0.005 mol % *versus* 5,0–10, 0 mol % in the previous work). Dienoate **1** was formed as the major product, however, CM product **3**, SM product **4** and anethole (**5**, originated from estragole isomerization) were also observed. Among the four possible geometric isomers of **1**, only the 2*E*,4*E* (hereafter named *E,E*) and the 2*E*,4*Z* (hereafter named *E,Z*) were formed. The isomers 2*Z*,4*E* and 2*Z*,4*Z* were not observed by GC analysis or in the NMR spectra of isolated dienoate **1** (Figs. S3-S8 in SI). The *E,E/E,Z* ratios diminished as the catalyst loading decreased. At higher amounts of G2, a 23/1 *E,E/E,Z* ratio was observed, corresponding to a diastereoselectivity towards **1**-*E,E* of 96 % (Table 1 - entry 1), while at lower loading, the *E,E/E,Z* selectivity experienced a small decrease, affording 93 % of **1**-*E,E* (*E,E/E,Z* equal to 13:1, Table 1 - entry 6). As the catalyst loading decreased, the overall selectivity towards **1** diminished from 60 % (Table 1 - entry 1) to 53 % (Table 1 - entry 6), while the selectivity towards **4** experienced a near two-fold increase (from 9 to 20 %). At higher catalyst loadings the primary *E,Z*-product can be recycled to the thermodynamically more stable *E,E*-product, as well as the self-metathesis product **4** can be recycled to **1** or **3**, enhancing the amount of these products at the end of the reaction. Nevertheless, the excellent productivities observed at lower catalyst loadings (up to 10,200) stimulated the investigation of other reaction parameters in attempts to improve the yield and selectivity of **1** under these conditions.

It is well known the cross metathesis partners molar ratio influences

Table 3
Solvent effects in the CM of estragole with MeSo.[a].

Entry	Solvent	Conv. (%)[b,c]	TON[d]	Selectivity (%)[c,e]			
				1 (*E,E/E,Z*)	3	4	5
1	toluene	60	12,000	53 (12/1)	23	13	8
2	*p*-cymene	63	12,600	54 (10/1)	23	13	8
3	dce[f]	63	12,600	60 (14/1)	18	10	9
4	Me-THF[g]	49	9800	50 (11/1)	26	14	8
5	MIBK[h]	10	2000	53 (10/1)	28	5	11
6[i]	toluene	64	12,800	58 (12/1)	20	12	8
7[i,j]	toluene	73	14,600	62 (13/1)	19	12	5

[a] Estragole (125 μL; 0.82 mmol, 1 equiv.), MeSo (660 μL; 4.92 mmol, 6 equiv.), estragol:MeSo molar ratio = 1:6, undecane (200 μL), G2 (0.041 μmol; 50 ppm), solvent (5.0 mL), 60 °C, 4 h.
[b] Conversions are based on estragole.
[c] Values are within ± 2 % deviation for duplicate reactions.
[d] TON = (mol of estragole converted)/(mol of catalyst).
[e] The selectivity of **2** remained within 1–2 % for all the reactions.
[f] 1,2-Dichloroethane.
[g] 2-Methyltetrahydrofuran.
[h] Methyl isobutyl ketone.
[i] 50 °C.
[j] 0.5 mL of solvent.

Table 4
Catalyst screening in the CM of estragole with MeSo.[a].

Entry	Cat.	Conv. (%)[b,c]	TON[d]	Selectivity (%)[c,e]			
				1 (*E,E/E,Z*)	3	4	5
1	G2	73	14,600	62 (13/1)	19	12	5
2	HG2	67	13,400	63 (16/1)	19	10	7
3	G2-^{i}Pr	48	9600	33 (10/1)	38	20	8
4	Ind2	63	12,600	53 (11/1)	25	14	7
5	RF2	48	9600	52 (9/1)	26	9	10
6	HG2-^{i}Pr	47	9400	34 (10/1)	37	21	8
7	HG2-tolyl	40	8000	70 (14/1)	17	7	6
8	HG2-Mes^{R}	53	10,600	64 (14/1)	19	9	7
9[f]	G2	89	8900	65 (14/1)	16	10	7

[a] Estragole (125 μL; 0.82 mmol, 1 equiv.), MeSo (660 μL; 4.92 mmol, 6 equiv.), estragol:MeSo molar ratio = 1:6, undecane (200 μL), Cat. (0.041 μmol; 50 ppm), toluene (0.5 mL), 50 °C, 4 h.
[b] Conversions are based on estragole.
[c] Values are within ± 2% deviation for duplicate reactions.
[d] TON = (mol of estragole converted)/(mol of catalyst).
[e] The selectivity of **2** remained within 1–2% for all reactions.
[f] 100 ppm of G2.

on the outcome of CM reactions. Albeit optimal results for several electron-deficient CM partners such as acrylates and acrylonitrile is accomplished in a 1:4 M ratio, other CM partners give better results in either lower or higher ratios, and thus this parameter must be investigated. In Table 2 the CM of estragole and MeSo was investigated in molar ratios ranging from 1:2 to 1:10, and a increase in estragole conversion was observed, reaching a maximum conversion of 69 % when using a ten-fold excess of the CM partner (for other molar ratios, see also Table S1). Not surprisingly the proportion of the self-metathesis product was reduced with the increase in MeSo. Nevertheless, the selectivity towards formation of target **1** was almost unaffected, especially in ranges greater than 4-fold equivalents of MeSo with respect to estragole. Conversely, the amount of the other CM product **3** also increased with the increase of MeSo. Less obvious is the reason for the considerable increase in the catalyst stability: the TON increases almost 55 % from entry 1 to entry 5 in Table 2. These observations can be reconciled if one considers that the proportion of propagating Ru-species formed by the initial reaction of the catalyst with MeSo will increase with the increase in the concentration of this reactant. A direct consequence would be increasing the cross products in detriment to the self-metathesis product **4**. An indirect consequence would be reducing the rate of the catalyst deactivation by reducing, at least at the early stages of the reaction, the formation of the highly reactive Ru-methylidene species originated from the interaction of the catalyst with the terminal double bond of estragole.

Despite better results being obtained with a ten-fold excess of the CM-partner, further optimizations were carried out using a six-fold excess of MeSo because this value allows good conversion and TON with a not so large excess of CM partner employed. A screening of representative solvents was then performed. *p*-Cymene and 1,2-dichloroethane (dce) resulted in comparable performances to toluene, with a slight better selectivity for **1** observed in dce (Table 2 - entry 3). More polar solvents, Me-THF and the green solvent methyl isobutyl ketone (MIBK) resulted in poorer conversions. The screening of temperature (Table S2) and amount of toluene (Table S3) is presented in SI, and selected conditions were included in Table 3, entry 7, in which estragole conversion reached 73 % with selectivity for **1** of 62 %. Both from environmental and economic perspective, the better solvent is no solvent. Thus, it is remarkable that this reaction shows a better performance when the amount of solvent is reduced to the minimum necessary to dissolve the catalyst (c.f. Table 3, entry 7).

Additional investigation was performed under the optimized conditions using a series of ruthenium ylidene catalysts (Fig. 2). Rather surprisingly, Hoveyda-Grubbs catalyst HG2 underperformed G2, exhibiting smaller estragole conversion and yield for **1** (Table 4 - entry 1 vs. 2). Such behaviour appears to contradict a general trend in metathesis chemistry for acrylates and other more challenging electron-deficient olefins, in which phosphine-free catalysts, such as HG2, outperforms G2 under optimized, low-catalyst loading conditions. The test was repeated three times, including a different batch of HG2, and the better performance of G2 over HG2 showed to be consistent. A key point to account for the better performance of HGII-type over GII-type catalyst, *e.g.*, in acrylate cross metathesis, is the substrate-induced decomposition of the ruthenacyclobutane intermediate by an enolate formed upon nucleophilic attack of dissociated phosphine (PCy_3) on the acrylate (Michael addition) [40,41]. Nevertheless, many examples of G2 exhibiting equal or superior performances as compared to HG2 are found in literature, especially when more reactive substrates are employed [42]. In the specific case of CM of estragole with MeSo, the better performance of G2 may reflect the lower electronic deficiency, and thus the higher reactivity, of the MeSo γ,δ-unsaturation, as compared to acrylates and acrylonitrile C—C double-bonds.

The study was extended to other pre-catalysts (entries 3–8). Generally speaking, catalysts with bulkier N-heterocyclic carbene (NHC) ligands resulted in lower conversions and selectivity for **1** (c.f. entry 1 *vs.* 3; entry 2 *vs.* 6). Steric constrictions disfavour the coordination of the *trans*-disubstituted MeSo γ,δ-unsaturation with respect to the terminal C—C double bond of estragole, thus favouring the homocoupling. Similar behaviour was observed previously for the CM of estragole with methyl acrylate [9]. Conversely, the catalyst containing a NHC with lower steric hindrance (*i.e.* HG2-tolyl) favoured a higher selectivity for **1**, albeit the conversion was lower probably due to faster catalyst decomposition *via* bimetallic pathways (c.f. entry 2 *vs.* 7). Regarding the ylidene moiety in the pre-catalysts, it is more difficult to provide generalizations since both steric and electronic effects seem to play an important role. Under the reaction conditions employed, catalysts that usually present equivalent or superior outputs presented a significant lower performance (c.f. entry 1 *vs.* 4 and 5; entry 2 *vs.* 8) for the CM of estragole with MeSo. This exemplifies the importance of the catalyst screening in challenging transformations.

Upon the increasing the G2 loading to 100 ppm (Entry 9), the conversion of estragole reached 89 % and a combined 83 % selectivity for the CM products with a turnover number of 8900 was achieved. Such results compare favourably with those obtained when using 1000 ppm of G2 in the initial experiments (Table 1, entry 1). That is, after all the optimizations, a near ten-fold increase in the catalyst productivity was

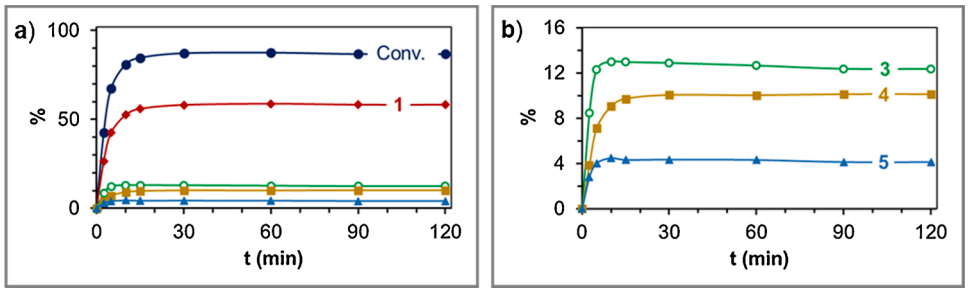


Fig. 3. Kinetic monitoring plot of estragole conversion (filled blue circles) and yield of CM products **1** (filled red diamonds) (a), and inset showing the yields (GC) for product **3** (unfilled green circles), **4** (brown squares) and **5** (light blue triangles) (b). Lines were added with the only purpose to aid visualization. Conditions: estragole (250 μL; 1.64 mmol, 1 equiv.), MeSo (1320 μL; 9.84 mmol, 6 equiv.), undecane (400 μL), G2 (0.164 μmol; 100 ppm), toluene (1.0 mL), 50 °C (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

attained with a smaller amount of the catalyst, with near identical estragole conversion and a slight improvement in the yield of **1**. Noteworthy is the chemoselectivity achieved for **1** in detriment of **2** under such low catalyst loadings, as opposed to reported literature values for similar products obtained from electron-rich olefins with ethyl sorbate (dienoate:enoate ratio = 8/1) and catalyst loadings as high as 10 mol% of G2 [15]. This represents a considerable improvement as not only the catalyst productivity was largely improved, but also it has been demonstrated that the use of electronic or steric 'protective strategies' when performing metathesis reactions with dienic substrates similar to methyl sorbate may be unnecessary. The presence of the ester functionality suffices for the chemodifferentiation of the olefinic units by second-generation metathesis catalysts. Under the optimized condition (Table 4, entry 9), a **1**:**2** ratio of 39:1 (97 %) was obtained.

To extract a more comprehensive set of information regarding the CM of estragole, with methyl sorbate, the progress of the reaction was monitored over a 2 h period (Fig. 3). The reaction proceeded fast over the first 15 min and remained virtually unchanged after the allotted time, which is a clear indicative of catalyst decomposition/deactivation. Moreover, evidence of consumption of neither the homocoupled product **4** nor CM product **3** leading to the formation of target CM **1** can be observed in the time-dependent plot, suggesting that the formation of these by-products, unless prevented, is difficult to be later remediated. Anethole (**5**), an estragole isomerization product, could also be observed from the beginning of the CM reaction, and its formation ceased as the metathesis reaction stopped (*i.e.*, after 15 min). This observation seems to rule out ruthenium hydrides or ruthenium nanoparticles as main isomerization species for this particular transformation, once such species would, *a priori*, keep this side reaction going on until complete estragole conversion. The isomerization mechanism proposed by Nolan & Prunet, in which the propagating {Ru = CHR} species is considered to promote C = C isomerization, appears fitting better the observed profile for the conversion of estragole into anethole [43,44].

4. Conclusions

The cross metathesis of estragole with the methyl ester of sorbic acid was investigated in detail employing low loadings of ruthenium-based second-generation metathesis catalysts. The corresponding dienoate **1** was formed as the major product, with high chemo- and diastereoselectivity, notwithstanding the concurrence of methyl homologation of estragole, as well as estragole self-metathesis and isomerization. The screening of the pre-catalyst allowed selecting G2 as a convenient pre-catalyst which, under optimized reaction conditions (catalyst 50 ppm, 50 °C and methylsorbate/estragole = 6), leaded to an excellent catalyst productivity and good selectivity for the desired product **1**.

CRediT authorship contribution statement

Leonildo A. Ferreira: Conceptualization, Investigation, Supervision, Writing - original draft, Writing - review & editing. **Josiane T. Silva:** Investigation. **Raissa G. Alves:** Investigation. **Kelley C.B. Oliveira:** Investigation. **Eduardo N. dos Santos:** Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors thank Conselho Nacional de Pesquisa Científica e Tecnológica - CNPq (INCT-Catálise) for financial support. Dedicated to Professor Pierre Dixneuf.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2021.118173.

References

[1] K. Grela, Olefin Metathesis: Theory and Practice, 1st edn, John Wiley & Sons Inc, 2014.
[2] E.N. dos Santos, A.V. Granato, A.G. Santos, in: M.M. Pereira, M.J.F. Calvete (Eds.), Sustainable Synthesis of Pharmaceuticals: Using Transition Metal Complexes as Catalysts, Royal Society of Chemistry, 2018, pp. 230–252, https://doi.org/10.1039/9781788010658-00230.
[3] T.T. Ho, T. Jacobs, M.A.R. Meier, ChemSusChem 2 (2009) 749–754, https://doi.org/10.1002/cssc.200900091.
[4] A. Rybak, M.A.R. Meier, Green Chem. 12 (2007) 1356–1361, https://doi.org/10.1039/B712293D.
[5] L.A. Ferreira, H.S. Schrekker, Catal. Sci. Technol. 6 (2016) 8138–8147, https://doi.org/10.1039/C6CY01181K.
[6] R. Duque, E. Ochsner, H. Clavier, F. Caijo, S.P. Nolan, M. Mauduit, D.J. Cole-Hamilton, Green Chem. 13 (2011) 1187–1195, https://doi.org/10.1039/C1GC15048K.
[7] A. Behr, S. Toepell, S. Harmuth, RSC Adv. 4 (2014) 16320–16326, https://doi.org/10.1039/C3RA47671E.
[8] A. Behr, J.P. Gomes, Z. Bayrak, Eur. J. Lipid Sci. Technol. 113 (2011) 189–196, https://doi.org/10.1002/ejlt.201000299.
[9] A.V. Granato, A.G. Santos, E.N. dos Santos, ChemSusChem 10 (2017) 1832–1837, https://doi.org/10.1002/cssc.201700116.
[10] J.A.M. Lummiss, K.C. Oliveira, A.M.T. Pranckevicius, A.G. Santos, E.N. dos Santos, D.E. Fogg, J. Am. Chem. Soc. 134 (2012) 18889–18891, https://doi.org/10.1021/ja310054d.
[11] J. Prunet, L. Grimaud, in: J. Cossy, S. Arseniyadis, C. Meyer (Eds.), Metathesis in Natural Product Synthesis: Strategies, Substrates and Catalysts, 1 edn, Wiley-VCH Verlag GmbH & Co, 2010.
[12] H. Bilel, N. Hamdi, C. Fischmeister, C. Bruneau, ChemCatChem 12 (20) (2020) 5000–5021, https://doi.org/10.1002/cctc.202000959.
[13] L. Ferrié, S. Reymond, P. Capdevielle, J. Cossy, Synlett. 18 (2007) 2891–2893, https://doi.org/10.1055/s-2007-990958.
[14] L. Ferrié, D. Amans, S. Reymond, V. Bellosta, P. Capdevielle, J. Cossy, J. Organomet. Chem. 691 (2006) 5456–5465, https://doi.org/10.1016/j.jorganchem.2006.09.026.
[15] T.W. Funk, J. Efskind, R.H. Grubbs, Org. Lett. 7 (2) (2005) 187–190, https://doi.org/10.1021/ol047929z.
[16] C.V. Krishna, V.R. Bhonde, A. Devendar, S. Maitra, K. Mukkanti, J. Iqbal, Tetrahedron Lett. 49 (2008) 2013–2017, https://doi.org/10.1016/j.tetlet.2008.01.055.

[17] E. Saraçi, L. Wang, K.H. Theopold, R.F. Lobo, ChemSusChem 11 (2018) 773–780, https://doi.org/10.1002/cssc.201701874.
[18] G. Moura-Letts, D.P. Curran, Org. Lett. 9 (1) (2007) 5–8, https://doi.org/10.1021/ol062017d.
[19] P. Dewi, S. Randl, S. Blechert, Tetrahedron Lett. 46 (2005) 577–580, https://doi.org/10.1016/j.tetlet.2004.11.154.
[20] H.-J. Jeon, K. Kim, Y.-D. Kim, S.-E. Lee, Appl. Biol. Chem. 62 (2019) 1–7, https://doi.org/10.1186/s13765-019-0471-z.
[21] R. Venkateshwarlu, B. Chinnababu, U. Ramulu, K.P. Reddy, M.D. Reddy, P. Sowjanya, P.V. Rao, S. Aravind, Med. Chem. Commun. 8 (2017) 394–404, https://doi.org/10.1039/C6MD00606J.
[22] Z. Oláh, D. Rédei, L. Pecze, C. Vizlar, K. Jóslay, P. Forgó, Z. Winter, G. Dombi, G. Szakonyi, J. Hohmann, Phytomedicine 34 (2017) 44–49, https://doi.org/10.1016/j.phymed.2017.06.006.
[23] R. Cookson, C. Pöverlein, J. Lachs, A.G.M. Barrett, Eur. J. Org. Chem. 21 (2014) 4523–4535, https://doi.org/10.1002/ejoc.201402205.
[24] A. Albrecht, J. Bojanowski, A. Kot, L. Sieron, Org. Biomol. Chem. 17 (2019) 4238–4242, https://doi.org/10.1039/C9OB00386J.
[25] M.J. Riveira, M.O. Marcariano, A. La-Venia, Org. Lett. 20 (2018) 4000–4004, https://doi.org/10.1021/acs.orglett.8b01567.
[26] R. Dada, Z. Wei, R. Gui, R.J. Lundgren, Angew. Chem. Int. Ed. 57 (2018) 3981–3984, https://doi.org/10.1002/anie.201800361.
[27] L.A. Marsili, J.L. Pergomet, V. Gandon, M.J. Riveira, Org. Lett. 20 (2018) 7298–7303, https://doi.org/10.1021/acs.orglett.8b03229.
[28] Z. Gao, S.P. Fletcher, Chem. Commun. 54 (2018) 3601–3604, https://doi.org/10.1039/C8CC01201F.
[29] D. Uraguchi, K. Yoshioka, T. Ooi, Nat. Commun. 8 (2017) 14793, https://doi.org/10.1038/ncomms14793.
[30] X. Wu, F. Xie, Z. Ling, L. Tang, W. Zhang, Adv. Synth. Catal. 358 (15) (2016) 2510–2518, https://doi.org/10.1002/adsc.201600375.
[31] Z. Wang, T. Kang, Q. Yao, J. Ji, X. Liu, L. Lin, X. Feng, Chem. Eur. J. 21 (2015) 7709–7712, https://doi.org/10.1002/chem.201500833.
[32] T. Sawano, A. Ashouri, T. Nishimura, T. Hayashi, J. Am. Chem. Soc. 134 (2012) 18936–18939, https://doi.org/10.1021/ja309756k.
[33] S. Okada, K. Arayama, R. Murayama, T. Ishizuka, K. Hara, N. Hirone, T. Hata, H. Urabe, Angew. Chem. Int. Ed. 47 (2008) 6860–6864, https://doi.org/10.1002/anie.200801928.
[34] K. Fukuhara, H. Urabe, Tetrahedron Lett. 46 (2005) 603–606, https://doi.org/10.1016/j.tetlet.2004.11.131.
[35] G. Herrán, C. Murcia, A.G. Csáky, Org. Lett. 7 (25) (2005) 5629–5632, https://doi.org/10.1021/ol0522485.
[36] S.G. Davis, G.D. Smyth, A.M. Chippindale, J. Chem. Soc. Perkin Trans. I (1999) 3089–3310, https://doi.org/10.1039/A907017F.
[37] C.R. Quijia, M. Chorilli, Crit. Rev. Anal. Chem. 50 (1) (2020) 62–77, https://doi.org/10.1080/10408347.2019.1573656.
[38] B. Salehi, Z.A. Zakaria, R. Gyawali, S.A. Ibrahim, J. Rajkovic, Z.K. Shinwari, T. Khan, J. Sharifi-Rad, A. Ozleyen, E. Turkdonmez, M. Valussi, T.B. Tumer, L. M. Fidalgo, M. Martorell, W.N. Setzer, Molecules 24 (2019) 1364, https://doi.org/10.3390/molecules24071364.
[39] Further conversion of the methyl ester to other functional groups, such as amides, can be accomplished using well-stablished literature protocols. For a green chemistry perspective on catalytic amide bond formation, see: M.T. Sabatini, L.T. Boulton, H.F. Sneddon, T.D. Sheppard, Nature Catal. 2 (2019) 10-17. https://doi.org/10.1038/s41929-018-0211-5.
[40] G.A. Bailey, D.E. Fogg, J. Am. Chem. Soc. 137 (23) (2015) 7318–7321, https://doi.org/10.1021/jacs.5b04524.
[41] A.G. Santos, G.A. Bailey, E.N. dos Santos, D.E. Fogg, ACS Catal. 7 (2017) 3181–3189, https://doi.org/10.1021/acscatal.6b03557.
[42] M. Bieniek, A. Michrowska, D.L. Usanov, K. Grela, Chem. Eur. J. 14 (3) (2008) 806–818, https://doi.org/10.1002/chem.200701340.
[43] D. Bourgeois, A. Pancrazi, S.P. Nolan, J. Prunet, J. Organomet. Chem. 643-644 (2002) 247–252, https://doi.org/10.1016/S0022-328X(01)01269-4.
[44] I.W. Ashworth, I.H. Hillier, D.J. Nelson, J.M. Percy, M.A. Vincent, Eur. J. Org. Chem. 29 (2012) 5673–5677, https://doi.org/10.1002/ejoc.201201036.